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Combustion of medium concentration CH_4-air mixtures in non-stationary reactors [+]

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Abstract

The aim of this paper is to study the combustion of medium concentration methane-air mixtures (in the range 5000-10000 ppmV, very interesting and usual in real emissions, but not widely studied in the literature) in unsteady-state reactors; the results obtained in a Reverse-Flow Reactor (RFR) and in a network of two (RN2) and of three reactors (RN3) will be compared. The influence of the main operating parameters, namely the switching time and the methane concentration in the feed, is investigated by means of numerical simulation, using an experimentally validated model. The performance of the three configurations is compared in terms of their stability intervals (values of switching time that allow for stable autothermal operation) and temperature profiles inside the reactor. The results obtained suggest that the RFR is the most appropriate choice for this application because of the wider stability interval, as well as because of the lower temperature variations inside the catalytic bed.

Keywords

Reverse-flow reactor, Simulated Moving Bed reactor, Reactors Network, Catalytic combustion, Methane combustion.

Introduction

The search of appropriate catalysts and combustion configurations for the catalytic combustion of methane in lean mixtures has became an interesting issue in the last years because of different reasons: among the others, there are many industrial emissions (from coke ovens, biological waste and wastewater treatment facilities, coal mines ventilation systems, etc) which contain small amounts of methane (up to 1%), which could be interesting energy sources because of the great flow-rates of these emissions. Moreover, methane is also very adequate as test compound for catalytic destruction studies, because it has the highest ignition temperature among paraffinic and aromatic compounds and, as a consequence, most pollutants will be destroyed at the temperature that allows for total methane combustion. Finally, the combustion of methane, and hence its transformation to carbon dioxide, is environmentally advantageous because the GWP (global warming potential) of methane is about 20 times higher than that of carbon dioxide.

In the traditional process the lean mixture of methane and air is fed to the catalytic reactor and some heat is required to carry the reactants to the temperature required to get full conversion; this is due to the low heat of reaction, which does not allow autothermal operation. The hot gases leaving the reactor can then be used to heat the cold reactants in a recuperative heat exchanger. Alternative configuration is the reverse-flow reactor (RFR), i.e. a fixed-bed reactor with periodical reversal of the feed direction that can allow autothermal operation even with low temperature feed and in presence of very low methane concentration in the feed (see, for example, the reviews of Matros & Bunimovich (1996), Kolios, Frauhammer & Eigenberger (2000) and of Litto et al. (2006)). Recently, Salomons et al. (2003) proposed the RFR concept for the treatment of lean methane-air mixtures (up to 0.3 % of methane) in vent gas

from coal mines.

Our Research Groups in Spain and in Italy were involved some years ago in a European Project (ENV4-CT97-0599) concerning the treatment of lean fugitive emissions from coke ovens. If the typical composition for an industrial plant is analysed, it comes out that methane is present in relatively high concentration; H_2O, H_2S, SO_2 and other compounds are also present in a lower concentration. The results we obtained appeared in various papers: we investigated the role of the physical and chemical properties of the catalyst (Fissore and Barresi, 2003), the simplified procedure for the design of the reactor (Cittadini et al., 2001a), the response to periodical variations in the feed (Cittadini et al., 2001b), the design of adequate control systems (Barresi and Vanni, 2002; Hevia et al., 2005) and of monitoring devices (Fissore et al., 2006) and the problem of the experimental investigation and of the scale-up of the results obtained in a bench-scale apparatus (Fissore et al., 2005). Finally, we have also compared the performance of packed bed and structured RFR (Marin el al., 2005).

The Simulated Moving Bed (SMB) reactor is another configuration which can be used to achieve multifunctional operation. Since the end of the 90s, Barresi's group at the Politecnico of Torino investigated a network of N catalytic reactors with periodical variation of the feed position, focusing the attention on gas-solid catalytic reactions, namely the catalytic combustion of lean VOC mixtures (Brinkmann et al. (1999), Fissore & Barresi (2002)), the low pressure methanol synthesis (Velardi & Barresi (2002)) and the synthesis gas production (Fissore, Barresi & Baldi (2003)). The main motivation for such researches belongs to the fact that in the SMB reactor the flow direction is never changed, thus avoiding the occurrence of wash out, i.e. the emission of unconverted reactants occurring in the RFR when the flow direction is reversed.

In all these papers a compact approach was proposed and all the N units are used: in the first interval the reactants are fed through unit 1, whereas the products exit at the end of unit N; in the second interval the reactants are fed through unit 2, whereas the products exit at the end of unit 1 and so on. The feed and the exit streams are adjacent in this configuration. Sheintuch & Nekhamkina (2005) proposed a different configuration where only N-1 units are used: in the first interval the reactants are fed through unit 1 and the products exit from unit N-1; in the second interval the flow enters at unit 2 and exits unit N, and so on. This approach requires fewer valves and tubes, but allows a less-efficient use of the catalyst.

The aim of this paper is to extend the analysis of the behaviour of the RFR and of the RN to the case of moderately high methane concentration in the feed (up to 1%): the two devices will be compared and the influence of the main operating parameter, i.e. the switching time, will be addressed. The comparison is done by means of numerical simulation, using an experimentally validated model, in terms of the intervals of switching time that allow for stable operation and of the evolution of the temperature inside the reactor. It should be also noted that, to the best of our knowledge, there are not systematic comparisons of these reactors for catalytic combustion processes, as in the case of equilibrium-limited reactions (Viecco & Caram, 2006).

Mathematical modelling

A one-dimensional heterogeneous model was used to investigate the influence of the main operating parameters on the stability of the RFR and of the RN; as the radial Biot number is very small, radial temperature gradients were neglected (the accuracy of this assumption has been recently discussed by van de Rotten et al. (2006)). Pressure loss inside the system was neglected and plug

flow, with dispersive transport of mass and energy, was assumed for the gas phase. The transient term was taken into account in the gas phase equations and in the energy equation for the solid phase, while the solid catalytic surface was considered to be in pseudo-steady state condition. The effect of the intraparticle mass transport was included in the model by means of the effectiveness factor. When simulating the RFR conventional Danckwerts boundary conditions are assumed in the ending sections of the reactor; in the case of the RN Danckwerts boundary conditions are assumed for the gas phase in each reactor and the continuity of gas temperature and concentration profiles are imposed between the reactors of the network (Velardi and Barresi, 2002). Details about the model equations and the correlations used to calculate the transport coefficients can be found in Fissore et al (2005). This model was experimentally validated in a bench-scale RFR, predicting fairly well both the behaviour at the periodic-steady state (in a wide range of operating conditions) and the dynamic evolution during the start-up and the extinction of the reactor (Fissore et al, 2005), as well as the effect of different wall materials (Hevia et al, 2006).

Results and discussion

The performance of both reactors types (conventional RFR and RN with two and three units) was studied considering that the reactor used for each device is of the same type, i.e. an adiabatic fixed bed reactor of 0.3 m of length and 0.014 m of inner diameter; the surface gas velocity is assumed to be equal to 0.1 m s^{-1}, thus giving a value of GHSV of about 2500 h^{-1}: due to the travelling hot wave, the hot zone moves in the reactor during the operation, thus requiring a lower value of GHSV (and thus a higher amount of catalyst) with respect to the usual catalytic afterburner, which are designed with a GHSV of 5000 h^{-1} (sometimes of

10000 h^{-1}). The reactor is assumed to be filled with catalyst particles (Pd/Al_2O_3) of spherical shape with a diameter of $7 \cdot 10^{-3}$ m. The physical properties of the reactor, as well as the kinetic parameters used in the simulations, are summarised in Table 1. The comparison was made in terms of the interval of switching time that allows for stable autothermal operation (with full methane conversion) and of the temperature profiles established in the catalytic bed. These profiles are important because the catalysts used for catalytic combustion are prone to thermal deactivation and fast temperature variations can affect both chemical and mechanical properties of the catalysts. The performance of the reactors was investigated in an interval of methane concentration of 1000 – 10000 ppmV. Most of the works reported in the literature deal with lower methane concentrations, up to 5000 ppmV (Fissore & Barresi, 2002); but concentrations around 1% of methane are nowadays of great practical interest, as said before, since these are typical in the emissions from coal mines venting systems and from many others industrial sites.

The stability intervals obtained in the RFR are shown in Figure 1, where the methane conversion as a function of the switching time is plotted. It can be observed that the stability of the reactor (the interval of switching time that leads to total methane conversion) increases as the methane concentration in the feed increases. The extinction of the reactor occurs because the zone at which the temperature is high enough to start the reaction moves out of the reactor before the flow direction is reversed. So, as the concentration of methane increases, the total amount of heat released is also increased and more time is required to move the high temperature zone out of the bed.

Concerning the RN, the stability interval is shown in Figure 2 for RN2 and in Figure 3 for RN3 and is much more complex than in the RFR; in particular, while in the RFR stable operation is possible even for very low values of t_c, in

the case of the RN a lower limit exists, below which no autothermal operation can be obtained. This different behaviour of the RN can be explained taking into account that the high temperature plateau should move a distance approximately equal to the reactor length in each switching period. So, when the feed point is changed, the gas will be fed to the hot zone, starting the reaction. Otherwise (in the case of lower switching times), the gases will be fed to a low-temperature zone, and combustion does not proceed, while the hot zone of the reactor will be cooled. Similar behaviour was reported by Fissore and Barresi in a previous work (2002), stating that RN leads to narrower stability limits than the RFR.

However, the presence of multiple stable intervals in the RN can be observed at the higher concentrations considered in this work. In the case of RN2 a unique and very narrow stability range is observed at 1000 ppmV (in good agreement with the behaviour reported in the literature), while at 5000 and at 10000 ppmV two different stability intervals are observed. The width of the interval observed at higher switching times increases as the methane concentration increases. This result (caused by the highest amount of heat released to the system) suggests that an increasing amount of methane leads to more stable operation, being very difficult to work below 5000 ppmV with RN technologies (the stability range is too narrow to ensure a stable operation). It must be also noted that the lower limit of this stability interval does not depend significantly on methane concentration, whereas this dependence is important in the upper limit. This result suggests that the lower limit of this zone is determined by the convective transport of the hot temperature wave, which depends on the reactor geometry and gas surface velocity. For the higher limit, the conductive heat transmission in the direction of flow plays an important role; thus, as the methane concentration increases, the maximum temperature

increases and the heat transport also increases (because of higher temperature gradients).

One of the main findings of this work is the presence of another stability interval at low switching times. This interval is clearly observed for the highest methane concentration studied (10000 ppmV), being observed for both networks of two and three reactors. It should be also noted that at this concentration it is possible (as in the case of the RFR) to work at very low switching times, without the escape of unconverted hydrocarbons which can occur in the RFR. In the studies carried out with 5000 ppmV of methane it is observed that the stability zone located at low values of t_c disappears in the network of three reactors, whereas a sequence of very narrow stability intervals is observed for the network of two reactors. In any case, the stability intervals observed for the RN2 are not useful for operation because of the narrowness of these intervals. The high-frequency stability interval is caused because the heat released in the combustion in the first reactor is enough to ensure that the reactants will circulate unalterated through the second (and third in the case of RN3) reactor when the feed is switched to the second reactor. So, the reaction will start in the first reactor (the last reactor after the switching).

Another remarkable feature of the stability intervals is that the proximity of the low- and high-frequency intervals decreases as the methane inlet concentration increases. However, a unique and wide stability interval could occur for these devices at very high concentrations (higher than 10000 ppmV) , but these conditions are not usual for this kind of applications.

One of the main constraints found in the catalytic oxidation processes is that the most active catalysts (such as palladium based catalysts) suffer thermal deactivation at temperature normally encountered in these kinds of processes. However, operation with noble metal catalysts is often preferred as they are

active at lower temperatures, leading to lower energy consumptions and being the reactor more likely to operate at autothermal conditions.

The influence of the switching time on the maximum temperature found in the reactor for the three configurations studied in this work is shown in Figure 4. The behaviour of the RFR and the RN is completely different. In the RFR, the maximum temperature in the bed decreases as t_c increases, with different slopes depending on the switching time interval, up to reactor extinction: in this case t_c is too high, thus the heat front is removed from the reactor and no autothermal operation can be obtained. As a consequence of this behaviour, the RFR should be operated at the lowest possible value of t_c which prevents catalyst overheating. Concerning the effect of the methane concentration, it is observed that higher concentrations lead to higher maximum temperatures in the bed; this behaviour is expected since the reaction is exothermic and is carried out in an adiabatic reactor.

Concerning the RN, very different behaviours are observed depending on the methane concentration. For the two lowest concentrations investigated, the maximum temperatures are slightly higher than those encountered in the RFR at the same switching time; moreover, the variation of the maximum temperature with the switching time is sharper than in the case of RFR: this is a consequence of the narrower stability interval. For the highest methane concentration, the maximum temperatures are slightly lower than those encountered in the RFR. In any case no significant variations are observed for this parameter for the three configurations studied in this work. However, it must be pointed out that the catalyst behaviour is not only affected by the maximum temperature found in the catalytic bed, but also by the presence of fast temperatures changes. These changes affect both the mechanical properties of the catalysts and the catalytic performance. Furthermore, it must be

considered the temperature profile at a given time and the evolution of the temperature with the time at a given position. The evolution of the temperature with the position in the catalytic bed is shown in Figure 5 for the RFR and in Figure 6 for the RN of three reactors. In the RFR (Figure 5) the temperatures profiles within the reactor just before two consecutive flow reversals are represented, working with the highest concentration of methane (10000 ppmV): high (t_c=450 s) and low (t_c=900 s) switching frequencies have been studied. In both cases, it was observed that the profiles are symmetric, i.e. the shape of the profiles within the reactor are periodically repeated, each twice the switching time. It is observed that the fraction of the reactor with high temperature increases as the switching time decreases; this is in good agreement with the increase of the maximum temperature of the bed with the decrease in switching time discussed above.

Concerning the RN (Figure 6), the temperature profiles have two important differences if compared with the RFR. The first one is that they are not periodically repeated with the switching times. So, it is possible to define the so-called temperature profile repetition period (TPRP) as the period of time that is needed for the repetition of the temperature axial profile. For the case of the RFR, for all the switching times, the TPRP will be always twice the switching time. In the case of reactor networks, the behaviour is different depending on the operation zone. So, in the low switching time zone, the TPRP/t_c ratio shows a strong variation with the t_c, as observed in the Table 2. In the high switching time region, the ratio between both parameters is constant and equal to 2 and 3, for RN2 and RN3, respectively. This means that the temperature profile moves to the distance corresponding to the reactor length in the switching period when working in the high switching times region, whereas in the low switching time region, it moves a shorter distance.

The most outstanding difference between the temperature profiles of the RFR and the RN is that in the last configuration, the temperature excursions are wider (from the temperature of the feed to the maximum temperature), and all the zones are affected. This is an important difference with the RFR (in this case the temperature of the central zone is almost constant) and this fact could be negative for the long term stability of the catalyst, since the thermal shock can affect both mechanical properties and activity of the catalyst. The portion of the reactor which is at low and high temperature varies depending on the switching time (Figure 6), being the width of the hot temperature region larger in the high switching time.

The last point to be considered is the temperature of the gases leaving the reactor. This parameter is important because is closely related with the temperature on the outlet of the reactor and, when working with the highest methane concentration, it determines the strategy for heat recovery. In the case of the RFR, and once the pseudo-steady state has been reached, the treated gases leave the reactor at relatively low temperatures, being this temperature almost constant with the operation time. By contrast, the temperature of the treated gases leaving the reactor networks varies with time, as observed in Figure 7 (RN2) and Figure 8 (RN3), where the evolution of the outlet gas temperature with the time (given as a fraction of the TPRP) is shown. In these figures it is observed, in good agreement with the results obtained for the temperature profiles inside the reactor, that the behaviour is different for the range of high switching time, when it is observed a periodicity of the temperature evolution, and the low switching time range, with a more complex and erratic behaviour.

Conclusions

The combustion of moderately high methane concentration streams (up to 1% of methane) in various non-stationary reactors has been investigated in this paper. The RFR has been demonstrated to ensure a wider interval of switching time that allows for stable operation and an almost constant temperature profile is obtained in the central part of the reactor. The RN of two and three reactors exhibits a narrower stability interval and the catalyst suffers important thermal shocks during the operation. At moderately high inlet concentration (5000-10000 ppmV) another stability interval (at low switching time) appears for the reactor networks. Anyway, even if the stability range of this device is enlarged, the interest in the operation of the reactor with these values of switching times is poor due to the irregular and erratic behaviour of the system, and the even higher thermal shock that the catalyst has to bear in this later case.

Acknowledgements

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Notation

$c_{p,c}$	specific heat of the catalyst, J kg^{-1} K^{-1}
d_p	particle diameter, m
d_R	reactor diameter, m
E_a	activation energy of the combustion reaction, J mol^{-1}
k_0	frequency factor of the combustion reaction, s^{-1}
L	total reactor length, m
T	temperature, K
t_c	switching time, s
u	surface velocity, m s^{-1}
z	non-dimensional axial position (axial reactor coordinate/total reactor length)
y	molar fraction

Greeks

ε	bed void fraction
ε_p	particle void fraction
λ_c	thermal conductivity of the catalyst, J $m^{-1}K^{-1}s^{-1}$
ρ_c	apparent density of the solid, kg m^{-3}

Subscripts and Superscripts

G	gas phase
S	solid phase or solid surface
0	feeding conditions

Abbreviations

GHSV	Gas Hourly Space Velocity, h^{-1}

RFR	Reverse-flow Reactor
RN	Network of Reactors
RN2	Network of Two Reactors
RN3	Network of Three Reactors
TPRP	Temperature Profile Repetition Period

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steady state has been reached) in a RN3 (upper graph, t_c = 300 s: —o—: beginning of the period, —Δ— : after the first switch, —◇— : after the second switch, —□— : after the third switch; lower graph, t_c = 600 s: —◇— : beginning of the period, —Δ— : after the first switch, —□— : after the third switch; the inlet methane concentration is 10000 ppmV).

Figure 7 Time evolution of the outlet gas temperature with the time (expressed as a fraction of the TPRP) in a RN2 when the periodic steady state has been reached (–◇— t_c = 450 s; —□— t_c = 750 s; —O— t_c = 900 s; the inlet methane concentration is 10000 ppmV).

Figure 8 Time evolution of the outlet gas temperature with the time (expressed as a fraction of the TPRP) in a RN3 when the periodic steady state has been reached (—◇– t_c = 300 s; —□— t_c = 600 s; —O— t_c = 900 s; the inlet methane concentration is 10000 ppmV).

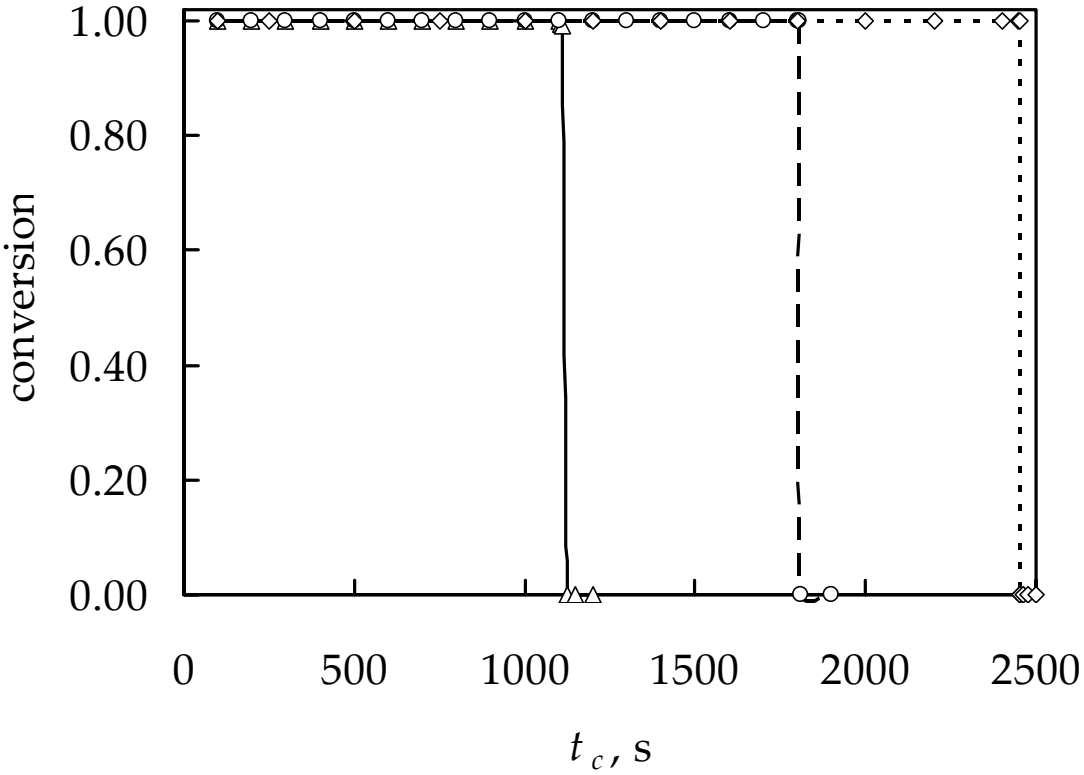
Table 1

u_0	0.1 m s^{-1}
L	0.3 m
d_R	0.014 m
d_p	0.0007 m
ε	0.35
ε_p	0.7
k_0	$1.625 \cdot 10^8$ s^{-1}
E_a	$9.124 \cdot 10^4$ J mol^{-1}
ρ_c	1000 kg m^{-3}
$c_{p,c}$	1000 J kg^{-1} K^{-1}
λ_c	0.18 W m^{-1} K^{-1}
$T_{G,0}$	20 °C
$y_{G,0} \cdot 10^6$	10^3 -10^4 ppmV

Table 2

t_c, s	*RFR*	*RN2*	*RN3*
100	2	18	21
200	2	142	87
300	2	2	6
350	2	6	21
450	2	14	-----
600	2	-----	3
750	2	2	3
900	2	2	3

Figure 1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conversion
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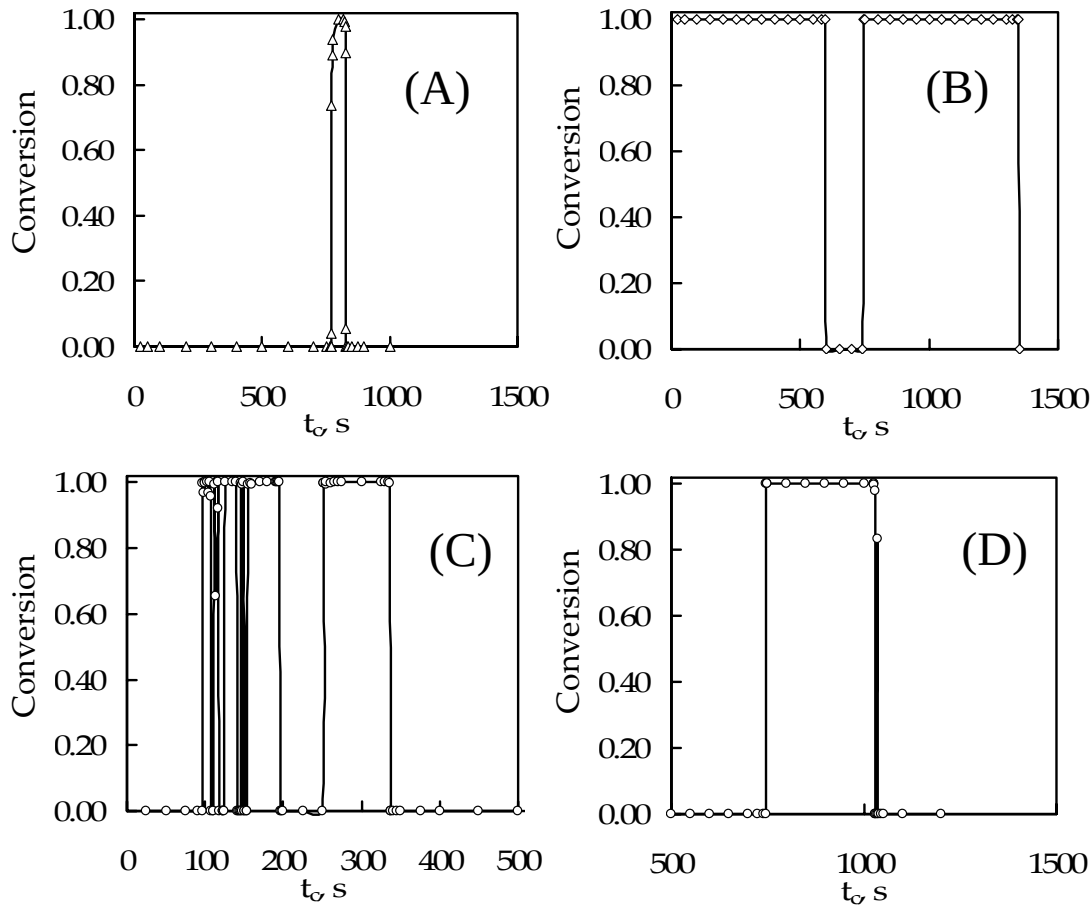
1500
2000
2500
t_c, s

Figure 2


(A)
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Conversion
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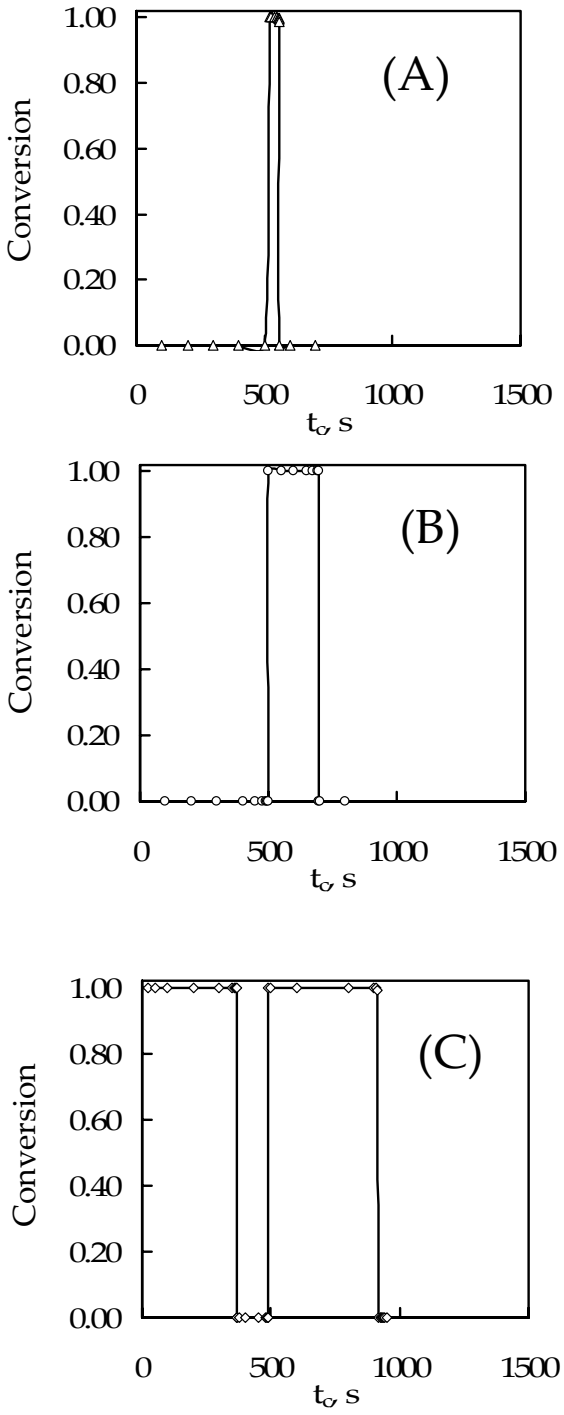
t_c, s

Figure 3



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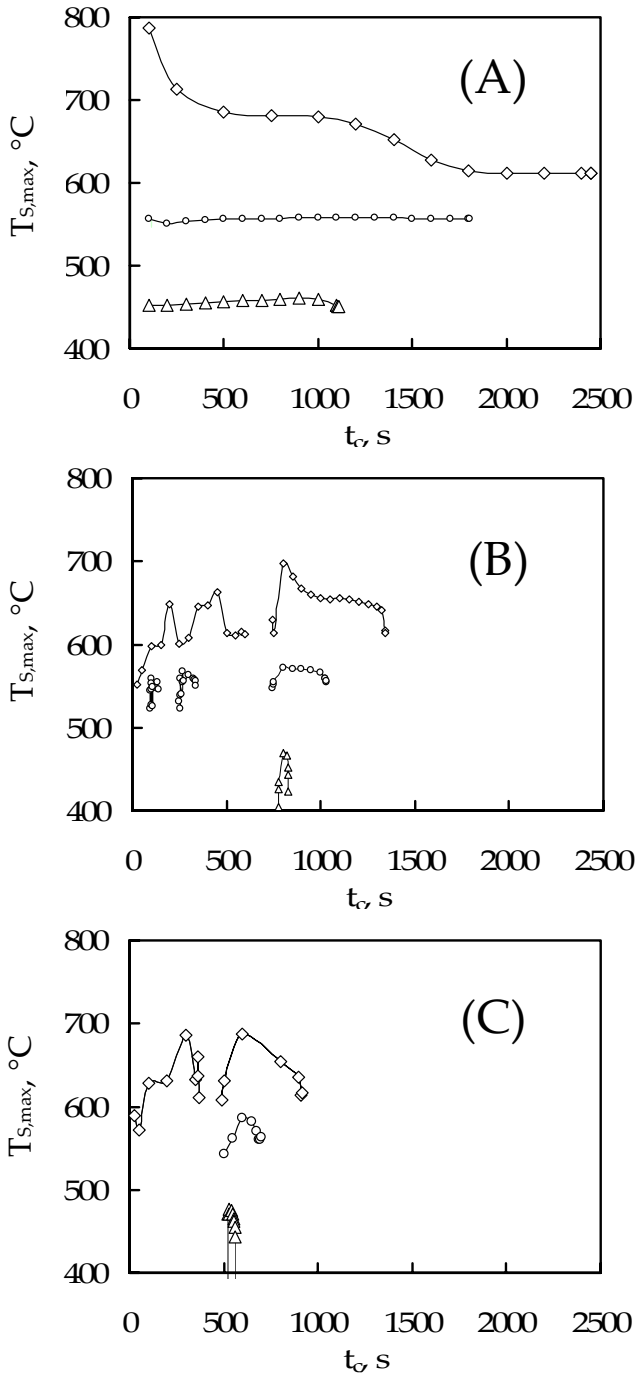

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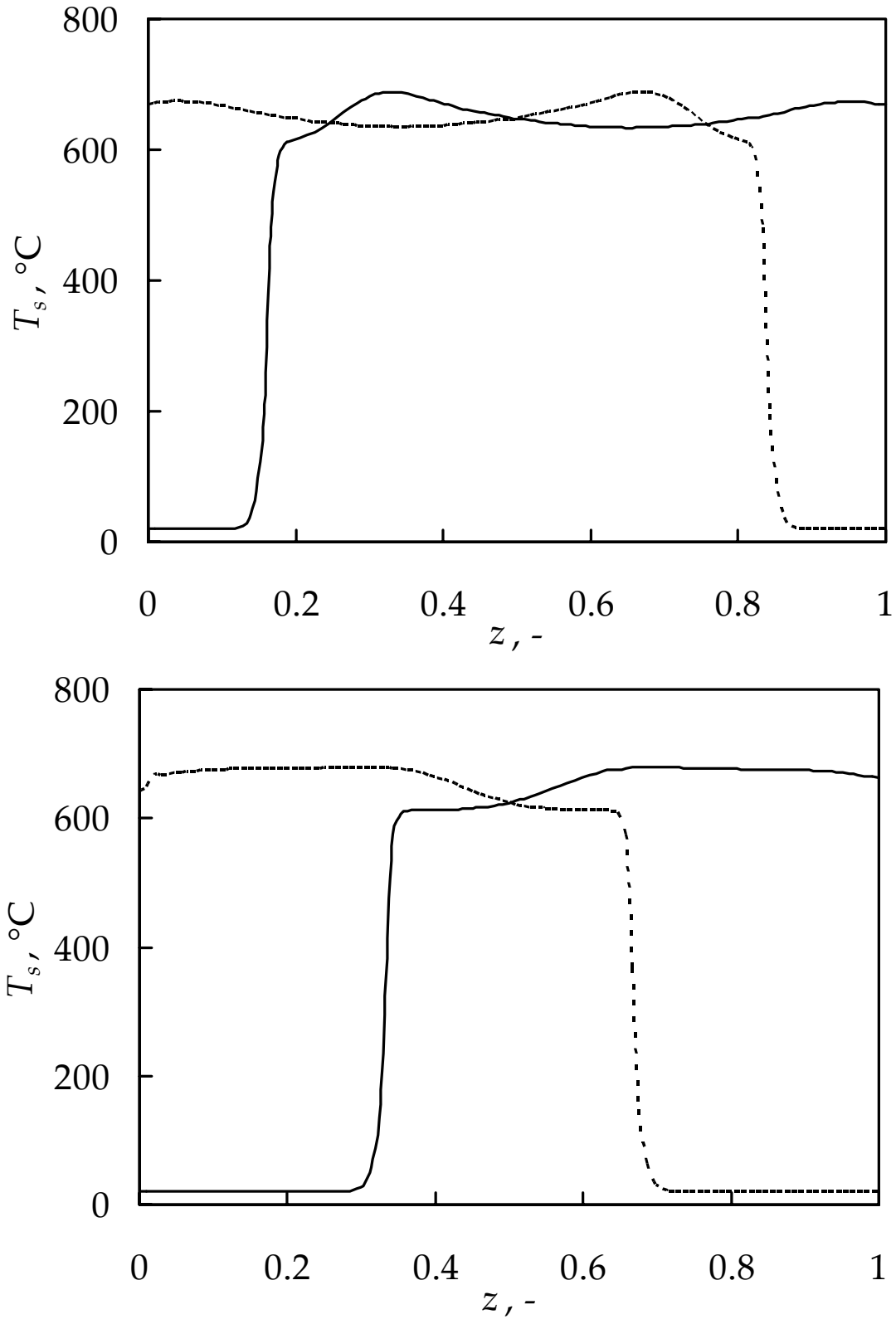
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Figure 6

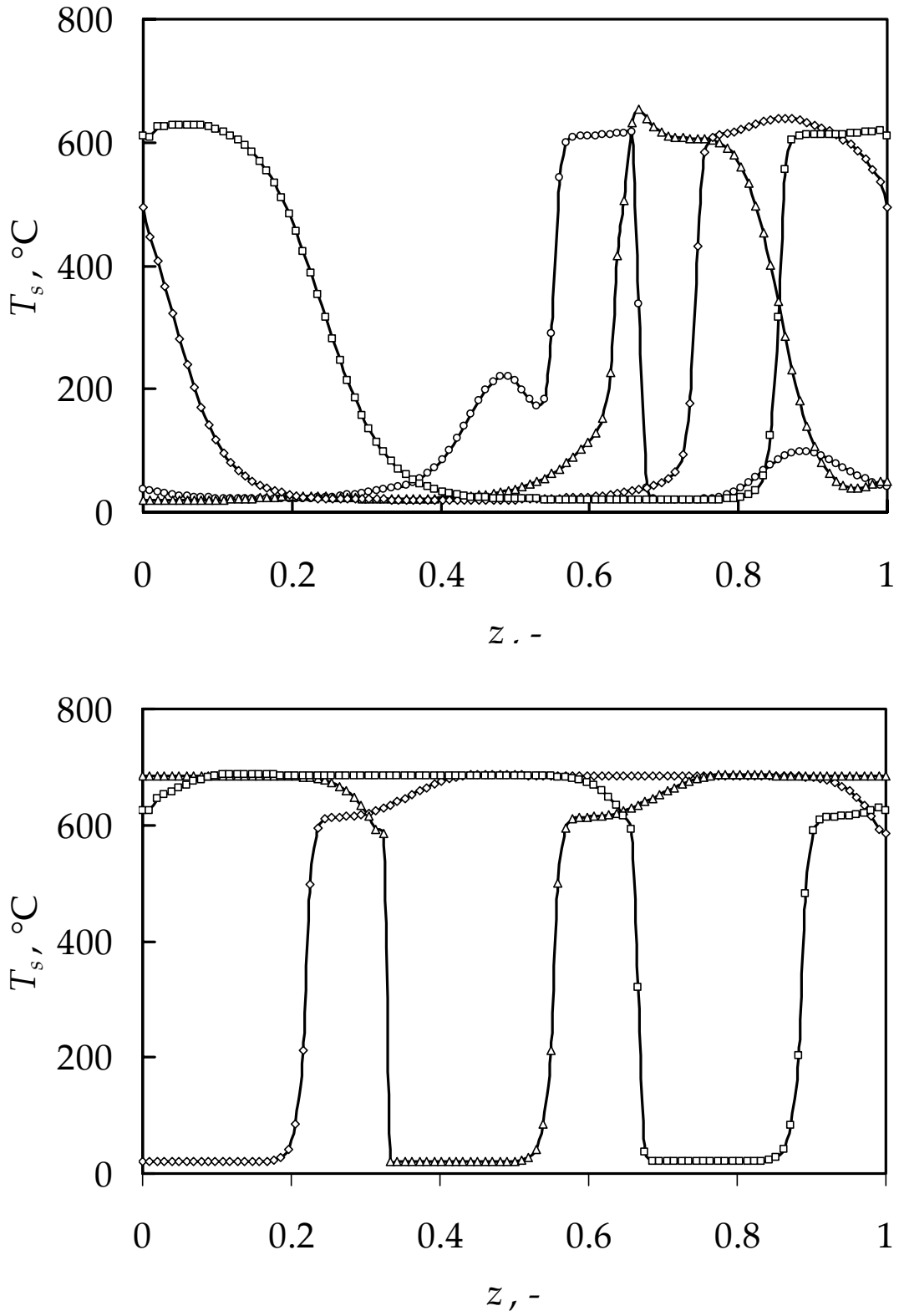
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Figure 7

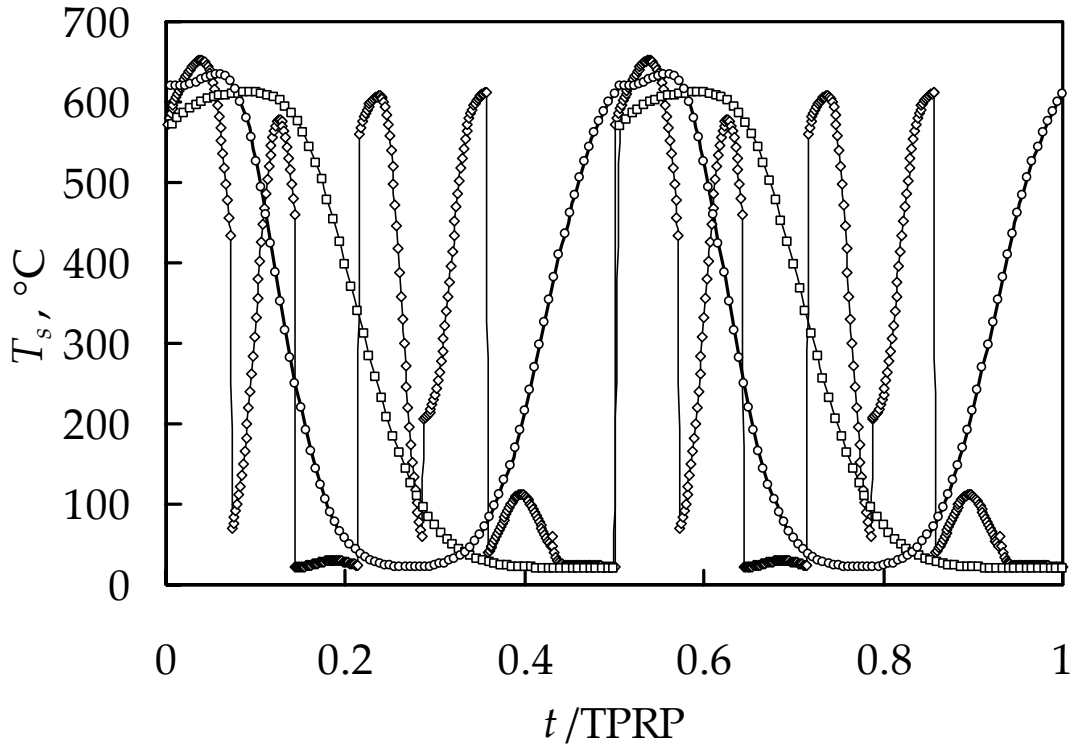

Figure 8